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(54) Method of applying a polymer film to a substrate

(57) A method of applying a film of a solid polymeric material to the surface of a solid substrate comprises causing relative frictional movement between the polymeric material (1) and substrate (3) to at least soften the contact surface of the polymeric material (1) and then moving the polymeric material (1) and substrate (3) in relation to each other, whilst continuing said relative frictional movement, so as to leave a trail (5) of the polymeric material on the substrate (3). In order to minimise problems of disintegration and ejection of the polymeric material a sleeve (2) is provided which surrounds the polymeric material adjacent the surface which will be contacted with the substrate.

Uses of the method include decoration, labelling and in the application of a potential adhesive.

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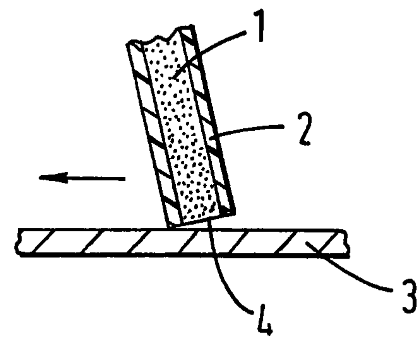

FIG.1

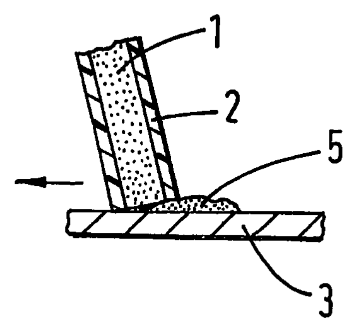

FIG.2

SPECIFICATION

Method of applying a polymer film to a substrate

This invention relates to a method of applying a film of a solid polymeric material to a substrate.

A known method of applying a film of a solid polymeric material to the surface of a solid substrate is described in British Patent Specification No. 1,579,433 in which relative frictional movement is caused between a substrate (of vulcanised rubber) and a polymeric material (thermoplastic plastics e.g. in the form of a rod), the relative frictional movement being sufficient to at least soften the contact surface of the polymeric material, and the polymeric material and/or substrate are then moved in relation to each other, whilst continuing said relative frictional movement, so as to leave a trail of the polymeric material on the substrate.

Using this type of method, various problems may be encountered, namely:

1) As the relative frictional movement is started, the cohesive properties of the polymeric material may be insufficient to prevent disintegration of the contact surface of the rod with the result that the rod wears away without a rise in temperature and thus cannot be successfully trailed along the substrate.

2) As the contact surface of the rod softens as a result of the frictional heat generated, softened polymeric material may be ejected. For example if the rod is spun against a substrate, softened polymeric material may be thrown outwardly because of the resulting centrifugal force. This effect means that polymeric material is wasted and in some cases so much of the polymeric material is ejected that very little remains to trail across the substrate. A further disadvantage is the mess resulting from the ejection of the polymeric material.

3) In order to successfully bond certain substrates it is sometimes necessary to buff the surface immediately before bonding. If the surface is buffed and then a significant time allowed to elapse before it is actually bonded, the buffed surface may be contaminated e.g. by dust or by chemical reaction, in which case little or no advantage will have been gained by the time-consuming buffing operation.

By using the method of the present invention in which a sleeve is provided on the polymeric material the aforementioned problems may be overcome. The sleeve surrounds the polymeric material adjacent the surface which will be contacted with the substrate. The sleeve is of a different composition to the polymeric material and should have the following properties:

1) Sufficient cohesive strength to withstand the initial frictional contact with the substrate before the surface of the polymeric material has softened. In this way the contact surface of the polymeric material can be kept in the initial frictional zone long enough for it to soften so that it can then be trailed across the substrate. This initial frictional contact between the sleeve and the substrate may result in buffing of the latter component which will often result in an improved level of adhesion. As the buffing operation takes place immediately prior to adhesion there is practically no chance for the newly buffed surface to become contaminated.

2) Sufficient cohesive strength at the temperature resulting from the frictional contact so that it will not, in the case of a spinning rod, be thrown outwards by the centrifugal force generated.

3) An abrasion resistance at the temperature resulting from frictional contact such that the sleeve will wear away at a sufficient rate to allow the softened polymeric material to be trailed on the substrate.

Preferably the sleeve also has sufficient impact resistance not to shatter as a result of initial frictional contact with a substrate.

By this method, polymeric films may be applied e.g. by way of decoration, labelling, a potential adhesive, or to confer desired properties on the surface of the substrate e.g. improvement in its compatibility with other materials, its ozone or general ageing resistance.

The material of the sleeve should of course be selected depending upon the particular polymeric material to be trailed. By way of example only, suitable materials for the sleeve may be thermoplastic materials (e.g. a vinyl chloride polymer, an acrylic polymer or a polyamide) and non-thermoplastic materials (e.g. a vulcanised natural or synthetic rubber, a resin such as an epoxy, urethane or acrylic resin, starch or paper). The sleeve may function as a carrier for additives to be incorporated into the film of polymeric material. For example, cross-linking agents which will react with the polymeric material could be incorporated into the sleeve so that frictional contact and application of the polymeric trail to a substrate will cause the cross-linking agents to mix with the polymeric material.

Examples of suitable polymeric materials to be trailed onto a substrate include a thermoplastic plastics (e.g. a polyester, a polyurethane, a polyamide or a polyolefin), an unvulcanised elastomer (e.g. a thermoplastic rubber such as an ABA type styrene/butadiene block copolymer, a polyurethane or a blend or graft of polyethylene or polypropylene with an EPDM or EP rubber, or a vulcanisable rubber such as natural rubber, polychloroprene or SBR), a resinous material (e.g. a zinc resinate, an epoxy, phenolic or hydrocarbon resin), and blends of any of these materials.

The sleeve may be applied to the core in a variety of ways e.g. by dipping a core in a solidifiable solution or dispersion of a material which is to form a sleeve and then solidifying (e.g. by drying) this coating. Alternatively a close-fitting sleeve e.g. of vulcanised rubber may simply be applied to a core. Examples of methods of making composites according to the present invention are:

i) co-extruding a polyurethane (e.g. as is available as DESMOCOL 530) with a vinyl

chloride/vinyl acetate copolymer so that the latter copolymer forms a sleeve around the polyurethane.

ii) dipping a core made from a blend of two different polyurethanes (e.g. DESMOCOL 420 and ESTANE 5712) in a polyacrylic adhesive, drawing the coated core through a die so that a uniform coating remains and then hardening the coating.

iii) wiping a core made from a blend of polychloroprene (e.g. available as Neoprene) and a phenolic resin with a solvent (e.g. toluene) so that the surface is rendered tacky, applying tissue paper to the tacky core and then allowing the assembly to dry.

iv) applying a length of natural rubber-based "bunsen burner tube" to a core material of natural rubber and a zinc resinate (e.g. available from Cray Valley Products).

v) dipping a core made from an SBR block copolymer (e.g. Cariflex TR 1101) and a hydrocarbon resin (e.g. Escorez 1071) into a prevulcanised natural rubber latex and then allowing the assembly to dry.

The relative proportions of sleeve and core material selected will usually depend upon a number of factors, namely whether the function of the sleeve is merely to constrain the spinning core in use or also to contribute to the formulation of the polymeric film e.g. by containing compounding ingredients. The relative proportions by volume per unit length of sleeve and core may be from 5%/95% respectively to 50%/50% respectively.

Where the polymeric material comprises a vulcanisable rubber this may be vulcanised after application to the substrate if desired. Usually the polymeric material will have a molecular weight of more than 15000.

Examples of suitable substrates include leather, synthetic leather (e.g. based on a polyurethane), wood, vulcanised rubber (foamed or unfoamed) and thermoplastic or thermoset plastics (foamed or unfoamed). Examples of suitable vulcanised rubbers include natural rubber, SBR, nitrile rubber and polyurethane rubber. If desired a vulcanised rubber composition which includes a high proportion of a resin (e.g. a hydrocarbon resin or a phenolic resin, such as t-butyl phenolic resin or terpene phenolic resin) may be used i.e. a so-called "resin rubber". Examples of suitable thermoplastic plastics include poly(vinyl chloride) and a polyurethane. The substrate may be reinforced e.g. by woven, knitted or non-woven fibres, such as of a nylon. Examples of synthetic leathers are synthetic poromeric (i.e. porous) leathers available as Porvair or Corfam. Suitable substrates include those materials used for making footwear e.g. an upper and/or a sole.

The polymeric material and/or sleeve and/or substrate may be in a compound with conventional ingredients such as plasticisers, vulcanising agents, waxes, tackifiers, softeners, fillers, pigments, anti-oxidants and stabilisers.

When the polymeric material consists of a polymer in composition with another ingredient or ingredients, the polymer is present in an amount of at least 20% by weight, preferably at least 30% by weight and advantageously at least 40% by weight. Often an amount of at least 70% is useful.

The polymeric material is not a "permanent tack" adhesive i.e. one which in solvent-free form is permanently tacky. Such materials will adhere instantaneously to most substrates by the application of only very slight pressure.

Where the polymeric material comprises a vulcanisable rubber and it is desired to vulcanise it after application to each of two substrates, a carrier layer including vulcanising agents may be sandwiched between the two applied polymeric films and then heat and/or pressure applied as necessary. Alternatively, vulcanising agents can be incorporated into the integral sleeve so that on frictioning the trail of polymeric material onto a substrate the vulcanising agents are mixed into it.

The relative movement between the polymeric material and the substrate may be produced in any convenient manner. One or both components may be moved. The friction may be achieved by rotary, angular or linear movement and may be continuous (i.e. in one direction) or oscillatory. An alternative to mechanical movement is the use of an ultrasonic frequency welding technique which creates rapid small vibratory movements between the surfaces.

The polymeric material may be in the form of a rod held in the chuck of a rotating or oscillating drill. When the surface of the rod in contact with the substrate has softened, which will generally be above 50°C and may be above 100°C in practice, the rod is moved across the surface of the substrate or vice versa so that a trail of the polymeric material is deposited.

The conditions of the relative frictional movement, such as speed and duration of the movement and pressure between the polymeric material and the substrate, are such as to at least soften the friction surface of the polymeric material and will depend upon the materials used. External heating is not usually necessary but may be employed if desired. Examples of suitable continuous relative rotary movement speeds are from 750 to 20000 revolutions per minute.

When an oscillatory movement is employed, this may be performed over a few degrees of arc or, in the case of linear movement, over about 0.1 to 6 mm, preferably 1 to 4 mm, and at a frequency of 50 to 200 Hz, especially 100 Hz.

A typical rate of frictional movement is between 2.5 and 10 m sec^{-1} and a pressure of usually only about 335 to 1340 $g.cm^{-2}$ (5 to 20 p.s.i.) is required. By comparison, prior known waxy hand-applied permanent-tack stick adhesives require a tip pressure in the order of 1340 to 6700 $g.cm^{-2}$ (20 to 100 p.s.i.) at a frictional movement rate of about 0.1 to 0.5 m sec^{-1}. Another contrasting factor is that by using the method of the present invention not only is the temperature of the polymeric material raised but so is that of the substrate and this facilitates the wetting action of the polymeric material thus improving the resultant bond strength.

Preferably the surface of the polymeric material to be contacted with the substrate is presented at an acute angle to the substrate trailed. This angle will accommodate the trailed polymeric material which might otherwise be squeezed out laterally. One such arrangement will now be described by way of example only with reference to the accompanying drawings in which:

Figure 1 is a cross-sectional view, at the moment of initial contact, of a substrate in contact with a spinning rod of polymeric material provided with a sleeve;

Figure 2 shows the components of Figure 1 after the polymeric material has been softened and trailed upon the substrate.

In Figure 1, a polymeric rod 1 surrounded by a sleeve 2 is held by means not shown at an acute angle to a substrate 3, and spun anti-clockwise. When the contact surface 4 of the rod has softened the rod is moved across the surface of the substrate 3 in the direction indicated by the arrow. The rotational movement of the rod is maintained during its traverse across the substrate and, as shown in Figure 2, a film trail 5 of polymeric material is left behind the rod.

Even if the contact surface of the polymeric material is heated by the frictional movement to a liquid state, because of the small proportion of material that is in this state it can be cooled very rapidly and therefore degradation of it or the substrate is unlikely.

If it is desired to reactivate the trail of the polymeric material, e.g. to use it as an adhesive to bond the substrate to another substrate, this may be done by using a suitable solvent or by heating the trail to soften it e.g. with infra-red, ultrasonic, radio frequency or induction heating methods or by a friction welding technique.

The polymeric material and/or the substrate may be frozen to harden it for the relative movement.

Separate films of polymeric material may be applied simultaneously by suitable equipment. Shaped films may be applied by using e.g. linear or angular friction techniques.

The substrate may be pre-treated, i.e. treated before the relative frictional movement between it and a polymeric material, to enhance its adherability to the polymeric film, for example the substrate may be pre-buffed or pre-treated with a chemical treatment agent e.g. aldehyde condensation resin-forming ingredients such as resorcinol and hexamethylene tetramine, acidified sodium hypochlorite, concentrated nitric acid, a chloroisocyanuric acid such as trichloroisocyanuric acid suitably as a solution e.g. in ethyl acetate or as a powder, an alkali metal salt of a chloroisocyanuric acid e.g. sodium dichloroisocyanurate (such salts are commercially available under the trade name 'Fi-clor') UV irradiation, glow discharge or naked flame. The term 'aldehyde condensation resin-forming ingredients' as used in this specification includes a partially condensed aldehyde resin. Alternatively and preferably a chemical treatment agent can be applied 'in situ' as the polymeric film is applied to the substrate. This can be done either by forming or drilling at least one cavity in the body of the polymeric material and packing the cavity or cavities with a treatment agent or by forming into the required shape e.g. by moulding a blend of a polymeric material and a treatment agent such as one of those already mentioned.

If desired the treatment agent may be supported in an inert medium e.g. a wax. When the polymeric material is in the form of a rod the cavity or cavities preferably extend longitudinally of the rod.

Incompatible substrates may be bonded by applying a polymeric film to each of them by the method of the present invention and then bonding the films e.g. by softening at least one of them and allowing the film or films to solidify in contact. Alternatively, an interlayer may be placed between the film-coated substrates and then the interlayer and usually also the films are softened and the assembly is allowed to cool.

The method of the present invention may be used in the manufacture of footwear. Generally, a footwear upper is of leather, synthetic leather, vulcanised rubber or thermoplastic plastics. The upper has to be attached to the sole of the article of footwear and previously this has usually been done using a proprietory adhesive. If the adhesive is based on a conventional rubber solution e.g. one based on polychloroprene, this usually must be coated onto the sole and upper and allowed to dry to a slightly tacky state before the two components are pressed together. If a polyurethane-based adhesive is used, this must usually be coated onto both components and dried completely before bonding. The adhesive layer on the sole is then softened, e.g. using an infra-red lamp, and the two components are pressed together. Both these methods are time-consuming because adhesive must be applied to sole and upper individually and the solvent in the adhesive allowed to evaporate before contacting the sole and upper. In addition it is usual to buff the adhering surfaces of the sole and upper before applying an adhesive.

It is proposed to have an upper comprising leather, synthetic leather, vulcanised rubber, thermoset or thermoplastic plastics having a layer or layers of a polymeric material bonded to it by the method of the present invention at places where the upper will eventually be attached to a sole. In order to attach the upper to a sole it is usually only necessary to soften at least the surface of the polymeric material, e.g. by infra-red, ultrasonic, radio frequency or induction heating methods, and press the softened surface against the sole which preferably also has had a trail of polymeric material applied to it. Alternatively the surface of the polymeric material may be softened by using a friction welding tool. On cooling, a bond is obtained between the upper and the sole. No messy solvents are involved, and the process of bonding the upper to the sole is quicker and easier as it is not usually necessary to apply a

trail of polymeric material to both upper and sole. Another advantage is that an upper can be easily transported already having a potential adhesive layer which can be bonded to a sole when required.

Examples of other applications of the method of the present invention are in the fabrication of harnessing, furniture, handbags, flexible or rigid containers and boats.

CLAIMS

1. A method of applying a film of a solid polymeric material to the surface of a solid substrate, characterised by causing relative frictional movement between the substrate and a composite of a core of the polymeric material surrounded by a sleeve coterminous with the contact surface of the polymeric material, said relative frictional movement being sufficient to at least soften the contact surface of the polymeric material and to wear away the sleeve adjacent said contact surface, and then moving the composite and/or the substrate in relation to each other, whilst continuing said relative frictional movement, to leave a trail of the polymeric material on the substrate.

2. A method according to Claim 1 characterised in that the relative proportions by volume per unit length of sleeve and core are from 5%/95% respectively to 50%/50% respectively.

3. A method according to Claim 1 or 2 characterised in that the molecular weight of the polymeric material is more than 15000.

4. A method according to Claim 1, 2 or 3 characterised in that the polymeric material consists of at least 30% by weight of a polymer in composition with at least one other ingredient.

5. A method according to Claim 1, 2 or 3 characterised in that the polymeric material consists of at least 40% by weight of a polymer in composition with at least one other ingredient.

6. A method according to Claim 1, 2 or 3 characterised in that the polymeric material consists of at least 70% by weight of a polymer in composition with at least one other ingredient.

7. A method according to any preceding claim characterised in that the temperature of the contact surface of the polymeric material is raised to more than 50°C by the relative frictional movement.

8. A method according to any of Claims 1 to 6 characterised in that the temperature of the contact surface of the polymeric material is raised to more than 100°C by the relative frictional movement.

9. A method according to any preceding claim characterised in that the rate of relative frictional movement is between 2.5 and 10 m sec^{-1}.

10. A method according to any preceding claim characterised in that the pressure between the polymeric material and the substrate is between 335 and 1340 $g.cm^{-2}$.

11. A method according to any preceding claim characterised in that the sleeve remains substantially stationary relative to the core during the relative friction movement.

12. A method according to Claim 11 characterised in that the sleeve is bonded to the core.

13. A method according to Claim 11 characterised in that the sleeve is a close fit to the core.

14. A method according to Claim 1 substantially as herein described with reference to Figure 1 or Figure 2.

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